

Solute and Temperature Effects in the Pervaporation of Aqueous Alcoholic Solutions

The phenomenon of pervaporation was first observed by Kober (1), who originated the term. It may be defined as the passage of a liquid through a semipermeable membrane and subsequent evaporation of the liquid. Farber (2) pointed out the usefulness of pervaporation in concentrating protein solutions. More recently, pervaporation and related phenomena have been discussed by da Fonseca (3).

Although the few available references cite the advantages of using pervaporation in certain chemical and biological researches, this technique has not been used to any great extent. In connection with food studies, we have used pervaporation to dehydrate mashed potatoes. Our methods may also be applicable in phases of other research—for example, in dehydrating plant tissue or in removing water from aqueous alcoholic extracts.

When a solution of equal parts by weight of ethanol and water was placed in a cellophane bag that was suspended in a forced-draft oven maintained at 60°C, the water content of the aqueous alcohol that passed through the membrane was about 65 percent. (The bags were formed from seamless, regenerated cellulose that is manufactured specifically for dialysis. Although wall thickness was not critical, a 0.0016-in. membrane was ordinarily used.) However, when a suspension of mashed potatoes in 1/1 ethanol-water was treated in the same manner, the water content of the pervaporated vapor was about 95 percent. Essentially the same result was obtained when the filtrate from a mixture of mashed potato, ethanol, and water was pervaporated, indicating that the higher ratio of water to alcohol must be due to the presence of the soluble potato solids.

Soluble potato solids consist principally of sugars, citric and other organic acids, nitrogen compounds, and inorganic salts. The naturally occurring mixture of water-soluble potato solids is also soluble in 1/1 ethanol-water but is only slightly soluble in ethanol.

To study the effect of the presence of a solute on the pervaporation of an aqueous ethanol solution, 1/1 ethanol-water mixtures containing various solutes (2.5 percent added) were pervaporated. Some of these solutes (class I) are soluble in ethanol and represent various degrees of solubility in water. Other solutes (class II) are soluble in water and are only slightly soluble in ethanol. The solu-

bilities of the various solutes in water and in alcohol and the percentages of water in the transmitted vapor are listed in Table 1.

Our class-I solutes included citric acid, hydroquinone, and benzoic acid; although citric acid is quite soluble in water, hydroquinone is moderately soluble, and benzoic acid is only slightly soluble. In pervaporating solutions containing class-I solutes, the percentage of water in the pervaporated vapor varied somewhat, increasing (but not proportionally) as the solubility of the solute in water increased. With citric acid added to the aqueous alcohol mixture, the water content (66 percent) of the pervaporated vapor was the same as that of the mixture without added solute. However, in the presence of the solutes that are only moderately or slightly solu-

ble in water, the water content of the pervaporated vapor was less than that of the control, being 64 and 59 percent for hydroquinone and benzoic acid, respectively.

Class-II solutes included dextrose, sodium chloride, and sodium citrate. The percentage of water in the transmitted vapor was much greater in every case with these latter solutes present than that in the control, being 81 to 82 percent for dextrose and sodium chloride and 96 percent for sodium citrate. In the presence of the class-II solutes, the percentage of water in the transmitted vapor apparently increases with progressive insolubility of the solute in ethanol.

A chamber was built to obtain more precise data related to the solute and temperature effects on the pervaporation rates of water and alcohol. It consisted of an aluminum cylinder 1 in. long with an inside diameter of 3.5 in., which was closed with membranes at the ends. Two aluminum rings with gaskets attached were used to clamp the cellophane membranes in liquid-tight seals. Two holes were provided in the wall of the cylinder, one for a reservoir tube and the other for a thermometer.

Experiments were carried out using water, ethanol, 1/1 ethanol-water, a 1/1 ethanol-water solution that contained 2 percent sodium citrate, and a 1/1 ethanol-water solution that contained 2 percent benzoic acid. Two temperatures, 25°C and 45°C, were utilized in a forced-draft oven. The pervaporation chamber was weighed, sampled initially, and sampled again after 3 hours. The percentage of water in the samples was determined by a modification of the Karl Fischer method (4). The pervaporating solution was stirred continuously by means of a magnetic stirrer. The data obtained are presented in Table 2.

Table 1. Relationship of solute solubilities (6) to percentage of water in pervaporated vapor.

Solute	Solubility (g/100 g solvent)		Water in transmitted vapor (%)
	In water	In ethanol	
Control			66
<i>Class I</i>			
Benzoic acid	0.29 (20°C)	52.5 (20°C)	59
Hydroquinone	7.2 (20°C)	49.8 (20°C)	64
Citric acid	163.4 (25°C)	62.1 (25°C)	66
<i>Class II</i>			
Dextrose	97.6 (23°C)	0.22 (23°C)	81
Sodium chloride	36.0 (20°C)	0.07 (18.5°C)	82
Sodium citrate	92.7 (25°C)	0 (25°C)	96

Table 2. Effect of temperature and solute on the pervaporation rates of water and ethanol.

Pervaporating liquid	Temperature (°C)	Pervaporation rate (g/in. ² hr)			Water (% in pervaporated vapor)
		Water	Ethanol	Total	
Water	25	0.42		0.42	
	45	1.31		1.31	
Ethanol	25		0.08	0.08	
	45		0.49	0.49	
1/1 Water-ethanol	25	0.32	0.34	0.66	48.5
	45	0.88	0.45	1.33	66.2
1/1 Water-ethanol (with 2 percent sodium citrate)	25	0.25	0.01	0.26	96.1
	45	0.81	0.02	0.83	97.6
1/1 Water-ethanol (with 2 percent benzoic acid)	25	0.15	0.24	0.39	38.5
	45	0.74	0.53	1.27	58.3

When ethanol and water are pervaporated separately, the ethanol-pervaporation rate increases more rapidly with a rise in temperature than does the water rate. However, when a 1/1 mixture of the two are pervaporated, different results are obtained. At the lower temperature, the presence of water enhances the passage of the ethanol, increasing its pervaporation rate from 0.08 to 0.34 g/in.² hr (Table 2). At the higher temperature, the rate of ethanol is approximately the same (0.49 to 0.45 g/in.² hr), regardless of whether water is present. The net effect of the temperature increase from 25° to 45°C, when a 1/1 aqueous ethanol solution is pervaporated, is to increase the percentage of water in the pervaporated vapor from 48.5 to 66.2.

The presence of 2 percent sodium citrate (water-soluble, ethanol-insoluble) in a 1/1 solution of ethanol and water decreases the ethanol pervaporation rate to a barely detectable level but decreases the water rate only slightly. The net effect is to increase the water content of the pervaporated vapor from 48.5 percent (control) to 96.1 percent, when one is operating at the lower temperature, and from 66.2 percent (control) to 97.6 percent at the higher temperature (Table 2).

The net effect of benzoic acid (water-insoluble, ethanol-soluble) is opposite to, but less pronounced than, that of sodium citrate. The water rate is reduced considerably, while the ethanol rate is reduced only slightly at the lower temperature and is even increased at the higher temperature. The net effect is a decrease in the percentage of water in the pervaporated vapor from 48.5 to 38.5 percent at

25°C and from 66.2 to 58.3 percent at 45°C (Table 2).

From thermodynamics, one would expect that the presence of a water-soluble, ethanol-insoluble solute would enhance the evaporation of ethanol from a water-ethanol mixture. An experiment involving evaporation from an open dish (no membrane) was conducted at 25°C, in which mixtures of equal parts of ethanol and water, with and without 2 percent sodium citrate, were evaporated for 6 hours in a forced draft (5).

As expected, the addition of sodium citrate resulted in a slight reduction of the water-evaporation rate (from 0.07 to 0.05 g/in.² hr) and a slight increase in the ethanol rate (from 1.05 to 1.10). Thus, interposition of a membrane at 25°C with sodium citrate present reversed the composition of the vapor from 96 percent ethanol to 96 percent water (Table 2). The total pervaporative rate of aqueous alcohol without solute present at 25°C (Table 2) was about half the total evaporative rate of the same mixture without a membrane.

The "solute effect" must be due to interfacial phenomena. The following explanation is postulated. As the solution is pervaporated, solute molecules either adhere to, or become trapped in, the membrane. Probably the latter is the case, since the solution is stirred vigorously during the pervaporation. The "good" solvent, by means of interaction with the solute molecules, can readily pass through the membrane. The "poor" solvent is repelled from the solute molecules, and its passage through the membrane is thus restricted.

If this hypothesis is correct, then a

membrane impregnated with solute should give a "solute effect" until the solute is gradually dissolved from the membrane if it is used in the pervaporation of a water-ethanol mixture. Conversely, if the solute is in the mixture and a clean membrane is used, the "solute effect" should increase with time. This was shown to be the case in two experiments. First, a membrane soaked overnight with a saturated aqueous solution of sodium citrate was used to pervaporate a 1/1 solution of aqueous ethanol. After 2 hours the water content of the pervaporated vapor was 82 percent, and at 4 hours it had dropped to 64 percent. Then a 1/1 aqueous ethanol solution containing 2 percent sodium citrate was pervaporated at 45°C for 8 hours, with hourly sampling. The ethanol rate, which was very low at the beginning, was reduced to zero by the third hour.

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References and Notes

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5. We wish to thank S. N. Timasheff of the Eastern Utilization Research Branch, U.S. Agricultural Research Service, for his valuable suggestions.
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